Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information

Sensitized Excited Free-Radical Processes as Read/Write Tools: Impact on Non-Linear lithographic Processes

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Synthesis of 1. 4-Hydroxy-TEMPO (120 mg, 0.7 mmol), Coumarin 343 (400 mg, 1.4 mmol), 1-(3-dimethylaminopropyl)-3ethylcarbodiimide hydrochloride (EDC•HCl, 340 mg, 1.8 mmol) and 4-Dimethylaminopyridine (17 mg, 0.14 mmol) were dissolved in 10 mL of CH_2Cl_2. The solution was stirred for 72h at room temperature, diluted with water (20 mL) and washed with aqueous HCl (0.5 M, 3 × 15 mL), saturated $NaHCO_3$ (3 × 15 mL) and saturated NaCl (2 × 15 mL). The organic phase was dried over $MgSO_4$ and the solvent was distilled off under reduced pressure. The residue was purified by column chromatography [SiO_2: $CHCl_3$/MeOH 19:1] to afford **1** (127 mg, 41%) as a yellow solid. MS: m/z 439 $[M]^+$. Anal. Calcd. For $C_{25}H_{31}N_2O_5$: C, 68.32; H, 7.11; N, 6.37. Found: C, 66.85; H, 7.28; N, 6.04.

Synthesis of 4. A solution of 4-Hydroxy-TEMPO (700 mg, 4 mmol), acetic anhydride (1.9 mL, 20 mmol), Et_3N (2.3 mL, 16.3 mmol) and 4-DMAP (50 mg, 0.4 mmol) in CH_2Cl_2 (20 mL) was stirred for 3h at room temperature under Ar, diluted with NH_4Cl and extracted with CH_2Cl_2 (3 × 25 mL). The organic phase was dried over $MgSO_4$ and the solvent was distilled off under reduced pressure to afford **2** (690 mg, 79%) as a dark red oil. MS: m/z 214 $[M]^+$. Anal. Calcd. For $C_{11}H_{20}NO_3$: C, 61.66; H, 9.41; N, 6.54. Found: C, 60.49; H, 9.56; N, 6.68.

Polymer films. For absorbance and emission measurements: 50 µL of a 30 µM solution of **1** was spin coated at 3500 rpm for 30s on a 1 inch quartz disk and dried at 140 °C for 10 min. For Fluorescence Lifetime Imaging and Total Internal Reflection microscopy: 50 µL of a 0.7×10^{-4} M solution of **1** was spin coated at 3500 rpm for 30s on a 0.17 mm glass slide (Fisher Scientific).

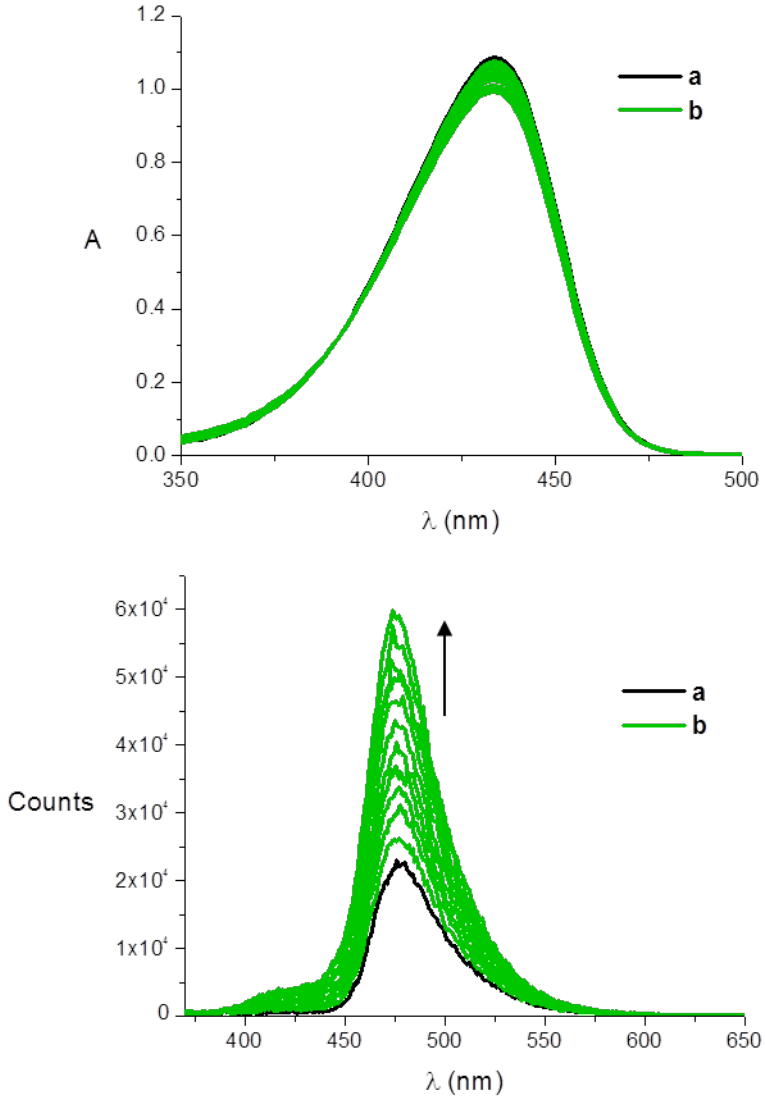

Figure S1. Absorption spectra of **1** (40 μM, MeCN, 25 °C) before (***a***) and after (***b***) LEDs irradiation (420 nm, 14.6 mW, 0–10 min). Emission spectra of **1** (40 μM, MeCN, 25 °C, λ_{exc} = 350 nm) before (***a***) and after (***b***) LEDs irradiation (420 nm, 14.6 mW, 0–10 min).

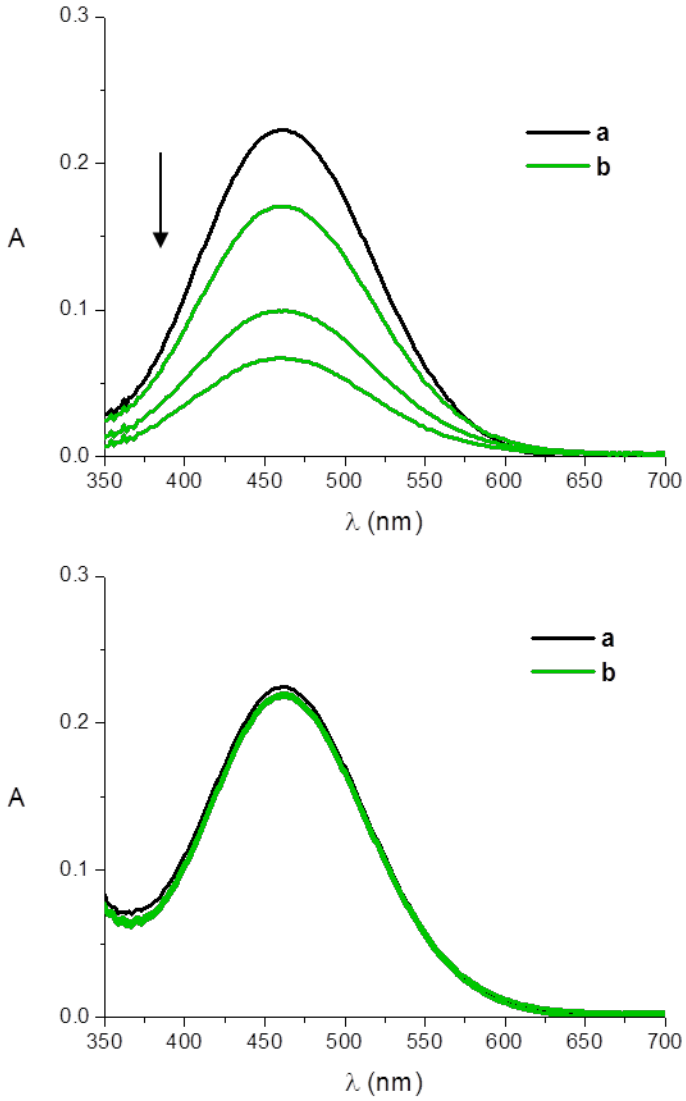

Figure S2. Absorption spectra of **4** (45 mM, MeCN, 25 °C) before (***a***) and after (***b***) irradiation with a xenon lamp (9 W, 0-15 min). Absorption spectra of **4** (45 mM, MeCN, 25 °C) before (***a***) and after (***b***) LEDs irradiation (420 nm, 100 mW, 0–20 min).

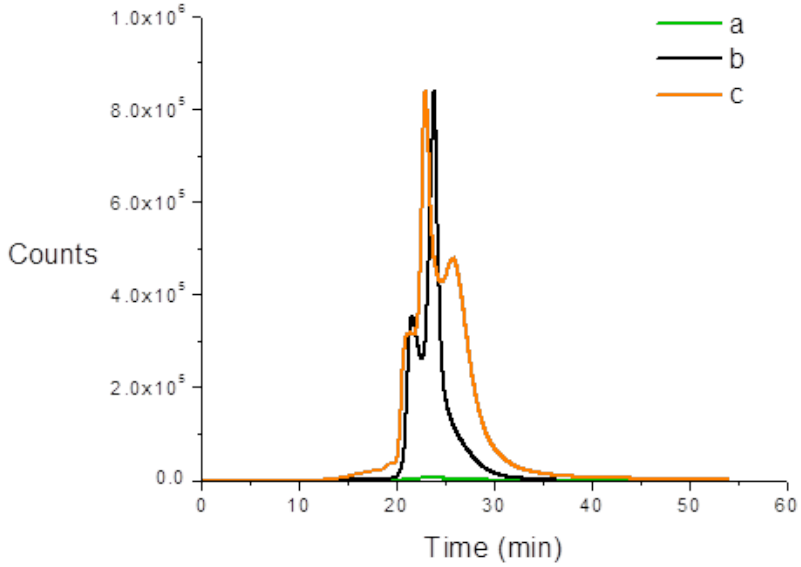

Figure S3. GPC analysis and fluorescence intensity (λ_{exc} = 350nm, λ_{em} = 460 nm) of a 30 μM of **1** in 10% PMMA before (***a***) and after (***b***) LEDs irradiation (420 nm, 14.6 mW, 0–10 min). The appearance of a band at 25.6 min corresponds to the concomitant formation of the **1**-PMMA adduct.

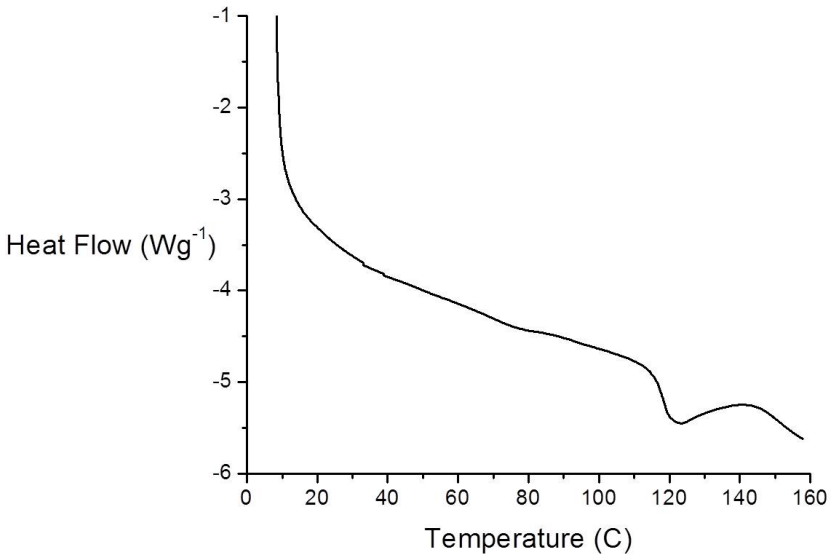

Figure S4. Differential scanning calorimetry of poly(methyl methacrylate). The glass transition temperature (T_g) was determined to be below 140 °C (temperature used to bake films to ensure that they were melted for "erasing" steps).

Analysis of Repeatability of the On/Off Cycles for Fluorescence Activation. Figure 5a shows the fluorescent image of a film containing **1** after irradiation through a lithographic mask. In order to evaluate the number of times a film can be irradiated and subsequently heated before losing all contrast, the images in Figure 5 of the main text were analyzed. In these samples, 50 % of the film is exposed while 50 % remains un-irradiated. The film is then heated above the T_g to allow the diffusion of fluorescence activated probe throughout the films. This increases the background signal in subsequent irradiations. After the second irradiation, an image is recorded again (Figure 5c). The average intensity of several regions of exposed and unexposed lines of Figure 5a are measured and the contrast is calculated as the ratio of intensity of exposed and neighbouring unexposed regions and is tabulated in Table S1 below. The average contrast for each irradiation is also shown in in Table S1. Assuming a ratio of 1 corresponds to zero contrast between background and exposed regions, we estimate a 30% loss in contrast in one on-off-on cycle. Therefore, the process could be repeated at least 3 times before losing all contrast. Nonetheless, no optimization has been done in effort to reduce background fluorescence, or to reduce irradiation time/intensity in order to obtain smaller overall changes in contrast that will allow for more cycles.

$$Contrast = \frac{Average\ Intensity\ Exposed\ Area}{Average\ Intensity\ Unexposed\ Area}$$

	Contrast 1st Irradiation (Figure 5a)	**Contrast 2nd Irradiation (Figure 5c)**
	1.43	1.40
	1.40	1.04
	1.51	1.10
	1.28	1.22
	1.13	1.26
		1.46
Average	1.35	1.25

Table S1: Average ratios of exposed VS unexposed regions of films shown in Figure 5.